

P1 1128401

# THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE  
United States Patent and Trademark Office

February 18, 2004

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE.

APPLICATION NUMBER: 60/432,089

FILING DATE: December 10, 2002

RELATED PCT APPLICATION NUMBER: PCT/US03/38748

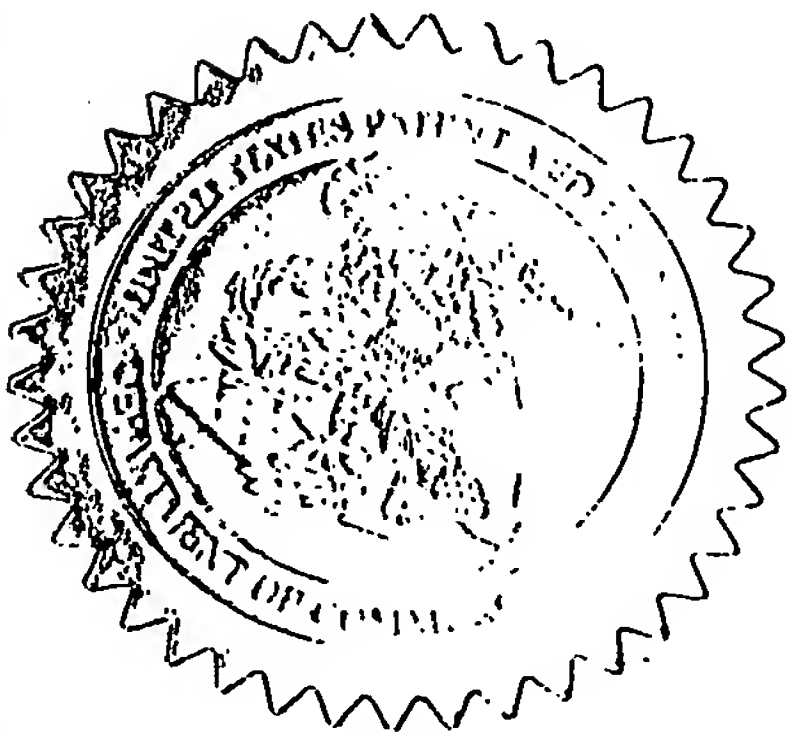
RECEIVED

23 FEB 2004

WIPO

PCT

By Authority of the  
COMMISSIONER OF PATENTS AND TRADEMARKS



*N. Woodson*  
N. WOODSON  
Certifying Officer

**PRIORITY  
DOCUMENT**

SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH RULE 17.1(a) OR (b)

BEST AVAILABLE COPY

BEST AVAILABLE COPY

12-11-02

12/10/02

12/10/02  
1036 U.S. PTO  
60/432089Approved for use through 10/31/2002. OMB 0651-0031  
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

**PROVISIONAL APPLICATION FOR PATENT COVER SHEET**

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Lab I No.

EL434047745US

INVENTOR(S)					
Given Name (first and middle [if any])		Family Name or Surname		Residence (City and either State or Foreign Country)	
Seamus Pulickel		Curran Ajayan		Latham, NY Clifton Park, NY	
<input checked="" type="checkbox"/> Additional inventors are being named on the _____ separately numbered sheets attached hereto					
TITLE OF THE INVENTION (500 characters max)					
Controlled Nanoscale Morphology for Non-Linear Optics [CNM-NLO]					
Direct all correspondence to: CORRESPONDENCE ADDRESS					
<input type="checkbox"/> Customer Number		Type Customer Number here		Place Customer Number Bar Code Label here	
OR					
<input checked="" type="checkbox"/> Firm or Individual Name		Rensselaer Polytechnic Institute			
Address		Attn: Office of Technology Commercialization			
Address		110 8th Street			
City		Troy	State	NY	ZIP 12180
Country		USA	Telephone	(518) 276-6023	Fax (518) 276-6380
ENCLOSED APPLICATION PARTS (check all that apply)					
<input checked="" type="checkbox"/> Specification Number of Pages		13	<input type="checkbox"/> CD(s), Number		
<input type="checkbox"/> Drawing(s) Number of Sheets			<input type="checkbox"/> Other (specify)		
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76					
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT					
<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.				FILING FEE AMOUNT (\$)	
<input checked="" type="checkbox"/> A check or money order is enclosed to cover the filing fees				\$80.00	
<input type="checkbox"/> The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number:					
<input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached.					
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.					
<input checked="" type="checkbox"/> No					
<input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: _____					

Respectfully submitted,

SIGNATURE



TYPED or PRINTED NAME Charles F. Rancourt

TELEPHONE (518) 276-6023

Date 12/10/02

REGISTRATION NO.

(if appropriate)

Docket Number:

RPI-775

**USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT**

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, D.C. 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C. 20231.

# **PROVISIONAL APPLICATION COVER SHEET** **Additional Page**

PTO/SB/16 (02-01)  
 Approved for use through 10/31/2002. OMB 0651-0032  
 U.S. Patent and Trademark Office, U.S. DEPARTMENT OF COMMERCE  
 Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Docket Number **RPI-775**

INVENTOR(S)/APPLICANT(S)		
Given Name (first and middle [if any])	Family or Surname	Residence (City and either State or Foreign Country)
Amanda Ganapathiraman	Ellis Ramanath	Troy, NY Clifton Park, NY

Number \_\_\_\_\_ of \_\_\_\_\_

**WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.**

## Controlled Nanoscale Morphology for Non-Linear Optics [CNM-NLO]

### ABSTRACT

This invention relates to SuperNanoMolecular (SNM) structures formed from carbon nanotubes with attached molecular species on the body of the tubes is then mixed with a polymer. The molecular species attached to the nanotubes is selected for its nonlinear optical properties. A polymer is produced from interfacial polymerization that is used to align the SuperNanoMolecular (SNM) (nanotubes and attached species) structures for potential waveguide, optical switching and other non-linear optical applications.

---

**Inventors:** Ajayan, Pulickel (RPI); Curran, Seamus (RPI); Ellis, Amanda (RPI);  
Ramanath, Ganapathiraman (RPI)

**Assignee:** RPI (Troy, NY)

**Appl. No.:**

**Filed:**

---

### References:

#### U.S. Patent Documents

<u>4985528</u>	Jan., 1991	Mignani <i>et al.</i>	528/59.
<u>5075409</u>	Dec., 1991	Barthelemy <i>et al.</i>	528/85.
<u>5098982</u>	Mar., 1992	Long, II	528/75.
<u>5231140</u>	Jul., 1993	Kilburg <i>et al.</i>	525/376.
<u>5266651</u>	Nov., 1993	Foss <i>et al.</i>	525/327.
<u>5290824</u>	Mar., 1994	Mandal <i>et al.</i>	525/293.
<u>5294463</u>	Mar., 1994	LeBarny <i>et al.</i>	427/488.
<u>5332520</u>	Jul., 1994	Bach <i>et al.</i>	526/318.
<u>5384378</u>	Jan., 1995	Etzbach <i>et al.</i>	526/298.
<u>5393644</u>	Feb., 1995	Etzbach <i>et al.</i>	526/273.
US 2002176650	Nov., 2002	Yiping <i>et al.</i>	

### Foreign Patent Documents

A-0 401 063	Dec., 1990	EP.
A-0 422 500	Apr., 1991	EP.
A-0 445 864	Sep., 1991	EP.
A-0 524 865	Jan., 1993	EP.
2630744	Apr., 1988	FR.
2246138	Jul., 1990	GB.

### Other Publications

- S. Curran *et al.*, Synthetic Met. (1999) 103, 2559-2562  
 J. Haremza *et al.*, Nano lett. (2002) 2, 1253-1258  
 O. Kulakovich *et al.*, Nano Lett. (2002) 2, 1449-1452  
 S. Banerjee *et al.*, Nano Lett. (2002) 2, 195-200  
 Z. Jin *et al.*, Chem. Phys. Lett. (2000) 318, 505-510  
 T. Lee *et al.*, J. Nanoparticle Res. (2000) 2, 345-362  
 D.J. Schiffrin, MRS Bulletin Dec (2001) 1015-1019

---

### *Claims*

---

What is claimed is:

1. The nanotubes have enhanced defect positions from either functionalization by pretreatment using plasma, ozone or ultra-sonication and then non-linear responsive molecules with specific luminescence tendencies are attached. These treated molecules (nanotubes and attachment to be known as SuperNanoMolecular (SNM) structures) are embedded into a solution where interfacial polymerization occurs and the SNM's are aligned
2. The nanotubes of (1) are mixed with a polymer, oligomer, monomer or luminescent molecule to enhance the optical properties of the nanostructure and this forms the SuperNanoMolecular (SNM) structure
3. The nanotubes can be preferentially coated with differing molecules to alter their absorption profile and hence their reactivity to differing light emissions
4. The SNM can be formed from metallic nanoclusters bound to the functionalized nanotube
5. The SNM can be formed from metallic nanowires bound to the functionalized nanotube
6. The nanoclusters used have an organic layer surrounding them to enable them to be bound to the nanotube body
7. The coatings of (1-6) that form the SuperNanoMolecular (SNM) structure can be either covalently, hydrophocically or electrostatically bound to the nanotubes or alternatively bound via van der Waals forces to keep the differing molecular structures in place
8. The SuperNanoMolecular (SNM) structures of (1-6) are aligned using interfacial polymerization
9. The process of (8) can include:
  - (a) Solubilizing the product in step (8) with another organic material to form a suspended phase; and
  - (b) Taking (a) and reacting with another organic component to produce a polymer surrounding the aligned nanotubes
  - (c) Taking (b) and forming a composite in the morphological manner of (i) a thin film, (ii) thread (iii) web (iv) suspended but soluble or insoluble pellet for future morphological and device applications
10. The process of claim 8 where
  - (a) The aligned nanotubes can be:
    - (i) Mixed with another organic solvent, that solvent using weak interactions such as van der Waals forces to maintain solubility
    - (ii) Mixed with an organic solvent containing a diacid or amine
  - (b) The polymerization follows pretreatment of one component of the polymerization step with carbon nanotubes
  - (c) The alignment of the tubes within the polymer matrix is a controlling factor for morphological design and applications

11. The SuperNanoMolecular (SNM) structures of (8) can also be composed of nanotubes with the attachment being a molecular structure that would enhance the entire non-linear optical properties
12. The nonlinear optical SuperNanoMolecular (SNM) structures of (8) can then be formed into an optical fiber in the format of (8, 9 & 10) composites
13. The nonlinear optical SuperNanoMolecular (SNM) structures of (8) can also be formed into a thin film in the format of (8, 9 & 10) composites for waveguiding ( $\chi^3$  effect)
14. The nonlinear optical SuperNanoMolecular (SNM) structures of (8) can also be formed into a thin film in the format of (8, 9 & 10) composites for optical switching ( $\chi^3$  effect)
15. The nonlinear optical SuperNanoMolecular (SNM) structures of (8) can also be formed into a thin film in the format of (8, 9 & 10) composites for waveguiding ( $\chi^3$  effect)
16. The nonlinear optical SuperNanoMolecular (SNM) structures of (8) can also be formed into a thin film, the thin film having electrodes through which an optical beam can pass through and be deflected, depending on the composite of (8, 9 & 10), formed using the materials nonlinear optical properties ( $\chi^2$  effect)
17. The nonlinear optical SuperNanoMolecular (SNM) structures of (8) can also be formed into thin film modulators and/or directional couplers and/or optical flip-flops

---

*Description*

---

## FIELD OF THE INVENTION

This invention concerns single and multi-walled carbon nanotube/organic molecular structures where the entire structure is a SuperNanoMolecular (SNM) structure that possesses different optical qualities. We use luminescent and/or quantum dots to attach to the nanotubes, these molecular structures possess strong non-linear and/or luminescent optical properties. These properties then enhance the SuperNanoMolecular (SNM) structures ability to act as the active optical component for nonlinear applications. Our invention allows the formation of flexible, durable and enhanced performance organic non-linear systems. The interfacial polymerization is used to align the nanotubes so that the SNM's are morphologically and hence opto-electronically controlled in film and fiber production. Control of the functionalization also allows control of the active sites along the nanotube body to take away the randomness of attaching molecules to the nanotube to form the SNM's.

## TECHNICAL BACKGROUND

Extensive research has been carried out on organic and polymer systems over the last decade to determine optimum optical and electrical properties for possible electronic and opto-electronic applications. Progress towards producing polymeric materials in a robust opto-electronic fashion creates a host of problems which include sensitivity to intensity (power) within the polymer, long term instabilities due to photo-chemical effects, low thermal and electrical conductivity (necessary for transport related functions), and relatively low third order effects. It has become clear that novel approaches to property tailoring in polymer systems are required to maximize the beneficial properties of the polymers while reducing their inherent deficiencies.

Carbon nanotubes have generated tremendous interest because of their unique combination of electronic, mechanical, chemical, and thermal properties. Potential applications reported have included chemical probes, sensors, hydrogen storage, nanopores, and memory storage. Nanotubes have extraordinary mechanical, electrical and thermal properties providing strong, light and tough physical characteristics. The tensile modulus and strength of some nanotubes ranges between 10 GPa to 1 TPa has been recently reported. The nanotubes exhibit an extraordinary performance compared with graphite and Kevlar fibers, and stainless steel. The nanotubes are at least 100 times stronger than steel, but only one-sixth as heavy, making it ideal to bolster all engineering materials. Moreover, the nanotubes have high thermal and electrical conductivities that are far better than copper. However, production techniques, material impurities and handling difficulties make nanotubes an intriguing yet problematic material to use on its own successfully in today's processes.

The present invention relates to the active materials in non-linear optics, which are used in particular in the field of optical signal telecommunications and optical signal processing. In more concise detail, these materials may be used for generating harmonics, frequency translation, optical memories, optical modulators, optical amplifiers, and other such non-linear light interaction phenomena.

Many materials have been proposed as suitable for non-linear applications. These include inorganic materials such as gallium arsenide and lithium niobate. However, in the past research has focused on polymerized organic materials which may be used in non-linear optics. These organic materials make it possible to manufacture multilayer integrated optical circuits by

techniques already tried and tested on electronic integrated circuits. However, processing inorganic materials is comparatively expensive and normally come in the form of monocrystals. Organic materials allow much faster signal processing than the inorganic materials, because of their much greater rate of change of state and ease of hybridization change. When looking at suitability, organic materials are ideal for optical modulators. It is possible to reduce the control voltage and the length of interaction between the light wave and the control electric field thereby allowing easier use and a greater flow of information.

The polymers which may be used in non-linear optics are generally used in film form. They are composed of a carbon skeleton onto which optically non-linear side groups or chromophoric groups are attached. In order for the material to be active in non-linear optics, it must be oriented so as to render the medium non-centrosymmetric. However, as orientation can lead to time dependent instabilities (samples degrade over time) these materials, in a practical sense, are unsuitable. However, combining nanotubes with such chromophores or side groups (inc. quantum dots) gives us the base material that is far more stable than previously used p conjugated systems.

The activity of SNM's in non-linear optics originates from the unusual combination of the nanotubes (SWNT or MWNT) and side attachments at the defect sites. These side attachments that come in the form of oligomers, monomers, dimers, atomic nanoclusters, nanowires, colloids and nanoparticles are defined here as chromophores, for our uses in this case. Chromophores must be understood as meaning any structural unit whose interaction with the electromagnetic field of light generates the desired optical effect. This effect can take place at resonant or non-resonant wavelengths. The activity of these chromophores in non-linear optics is given by their hyperpolarizability.

[01] One means of addressing some of the deficiencies of polymers in an electronic manner is the dispersion of nanostructures to create a polymer matrix that derives its electronic behavior from a cooperative behavior between the host and additive. The first work done in this area has resulted in extensive scientific interest resulting in a number of patents based on their electronic applications. Nanotubes have only recently been used as electrical or mechanical inclusions in a polymer matrix because of the difficulty in achieving efficient dispersion.

[02] This difficulty is primarily due to the non-reactive surface of pristine nanotubes. The first solubility for nanotubes was reported only 5 years ago where the polymer used (PmPV) also acted as a filter for nanoparticles resulting in a more purified sample of polymer and nanotubes in a composite. However, intrinsic van der Waals attraction among tubes, in combination with their high surface area and high aspect ratio, often leads to significant agglomeration, thus preventing efficient transfer of their superior properties to the matrix. Focus now must be on reducing the nanotube aggregation effect and dispersing the nanotubes in a more ordered fashion to enhance the overall macro properties of the host polymer.

[03] Carbon nanotubes can be formed in a variety of manners, from arc discharge to CVD. They can be purified also through a variety of methods from oxidative methodologies, attachments with sulphonic acids or simple plasma treatment. The resultant nanotubes are free of amorphous materials and polyhedra. Most carbon nanotubes end up with 'functionalized' sites on the nanotube body. These sites can be in the form of structural defects formation (in the case of pentagon and heptagon), or they can simply be  $sp^3$  formation and possessing dangling bonds.

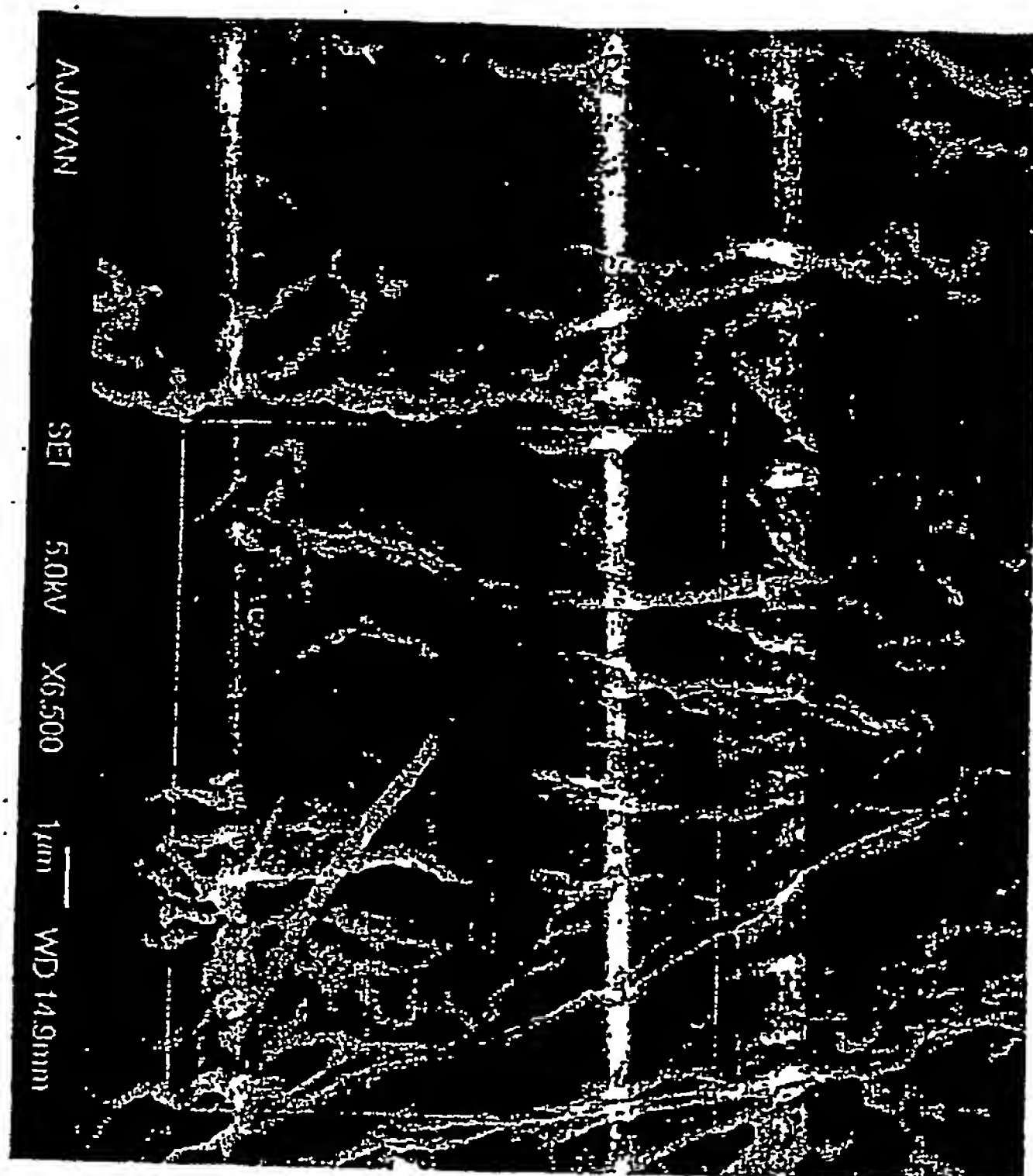
[04] We use these susceptible or reactive sites as positions to bring other molecules along and attach them to the nanotubes. These molecules can be in the form of large complex polymers (from conjugated to non-conjugated systems) or small molecules, even in the case of atoms such as Se, simply colloidal type structures. We can attach them onto the nanotubes, and using this enhanced molecular structure to tune the molecules for optical properties. In our case we are using molecules that have strong photo-absorptive tendencies in order to enhance the optical photoconductive effect.

[05] The primary aim of the work is to produce flexible highly efficient optical waveguides that can be used on any surface or substrate. This would allow them to be applied to any surface that received sufficient light for energy production without the cost of expensive mounts and cabling.

- [06] Another function of developing these SNM's is to control the morphology of the non-linear system. While others may attach nanoparticles to nanotubes, no effort has been made to control the morphology.
- [07] While others use random attachments in a non-controlled manner to attach molecule species to the body of the tubes, we manage to control the amount of functionalization and so also the attachments to the nanotube body
- [08] Random attachments on some individual SWNT's may be possible in a non-controlled manner, we can also control the amount of bundling that occurs in the nanotubes (either SWNT or MWNT) in a non destructive manner, so introducing control into a system that relied in the past on random statistical attachments.
- [09] Morphology control is so critical simply using nanotubes in a composite alone is insufficient to produce the required non-linear effect due to lower non-linear responses, as well as having no control on the scattering.
- [10] While nanotubes in themselves, whether in a composite or on their own may have a non-linearity, as reported by S. Curran years ago, we do not wish to rely on this native non-linearity, but to collectively enhance the region occupied by the SNM within a polymer (forming the composite) while controlling the morphology.
- [11] For telecommunications, control of the directionality of the SNM's is critical for aligning the optical field along the  $\pi$ -conjugated system as well as the nonlinear effects combined together to enhance the region around them.
- [12] We use either organic based materials and/or quantum dots attached to the nanotubes, then control the morphology of these structures to minimize dispersion and scattering of optical signals.
- [13] The polymer matrix is to be used as a protective and holding matrix as well as for alignment of the nanotubes themselves. The use of interfacial polymerization will allow fibers and thin films to be produced over any surface.
- [14] These molecules attached to nanotubes can also be used to create strong dipoles that would enhance the materials nonlinear optical properties. Nonlinear optics has many potential applications, not in the least telecommunications and information technology industry.
- [15] The presence of the SuperNanoMolecular (SNM) species enhances nonlinear optical properties and also enhances stability of the composite while considering the effects of high power laser coupling for waveguiding or transmission
- [16] The presence of the nanotubes in the formation of the SNM's also allows us to use stronger optical fields with a reduced degradation effect from those optical fields.

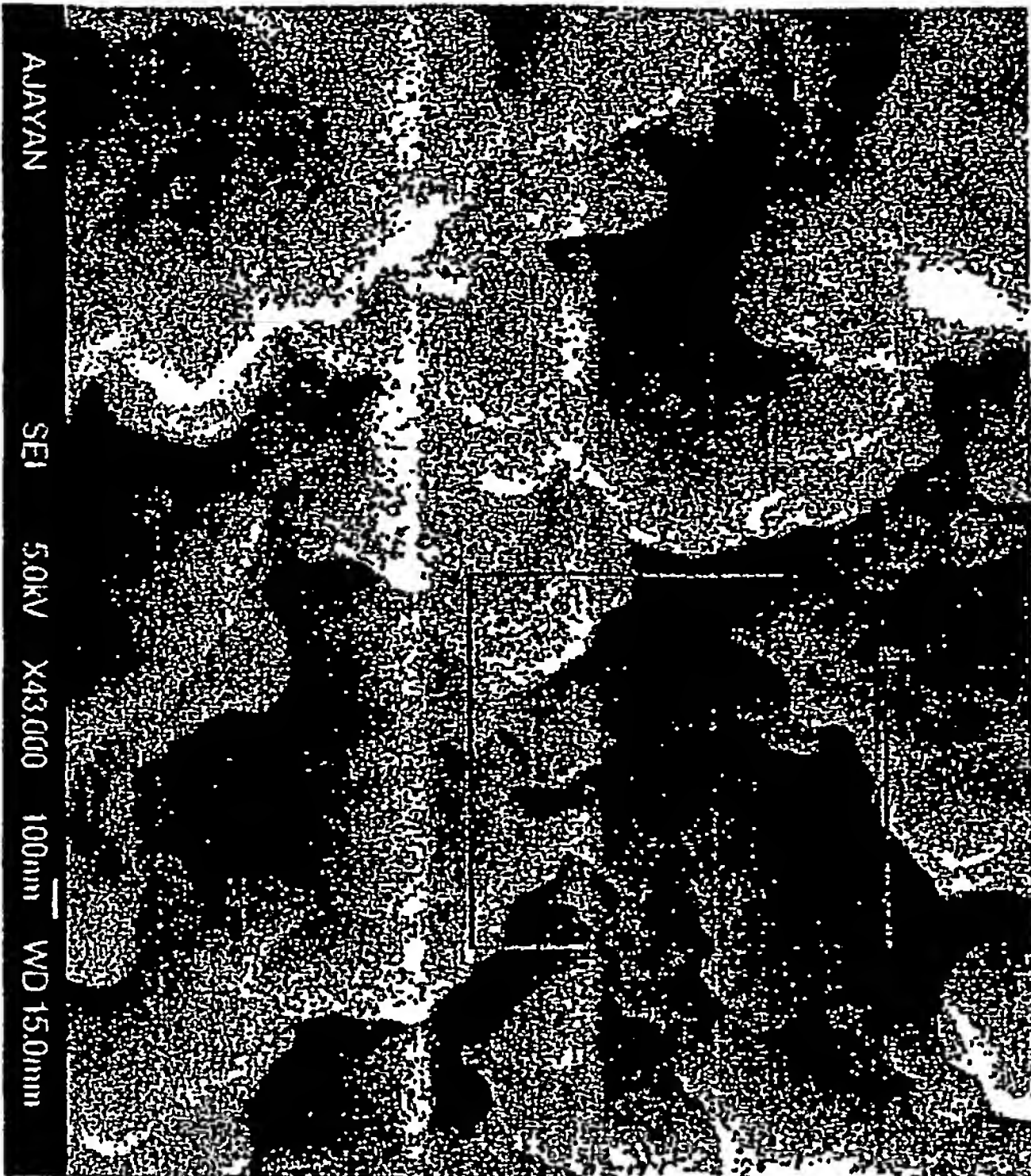
60432689.171002

Fig 1 : Nanotubes  
embedded in  
polymer



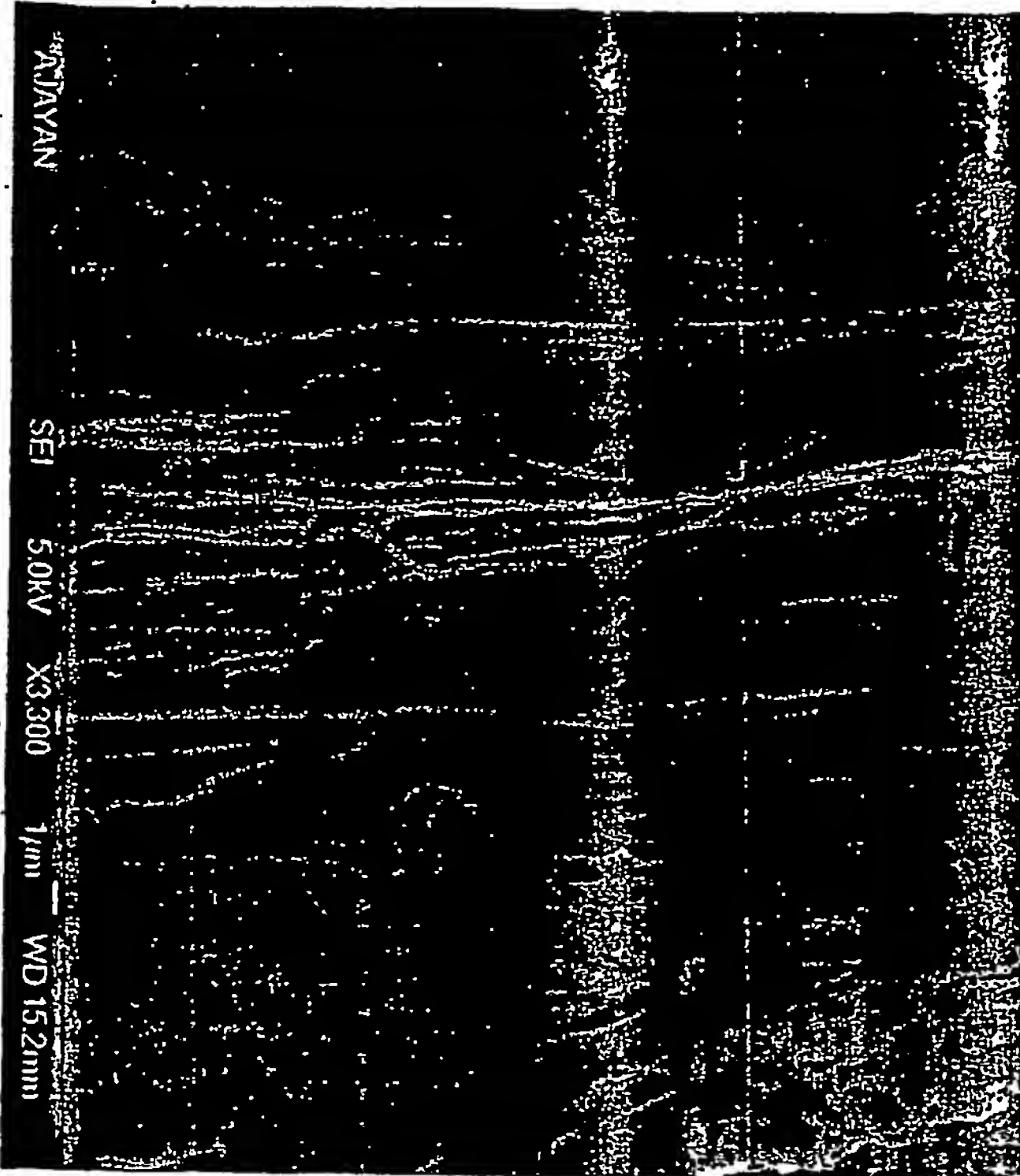
60432059.1E100E

Fig 2 : Nanotube emb  
in polymer



60432039 . 12.10.02

Fig 3: Nanotubes aligne  
along polymer fibre  
stretching direction



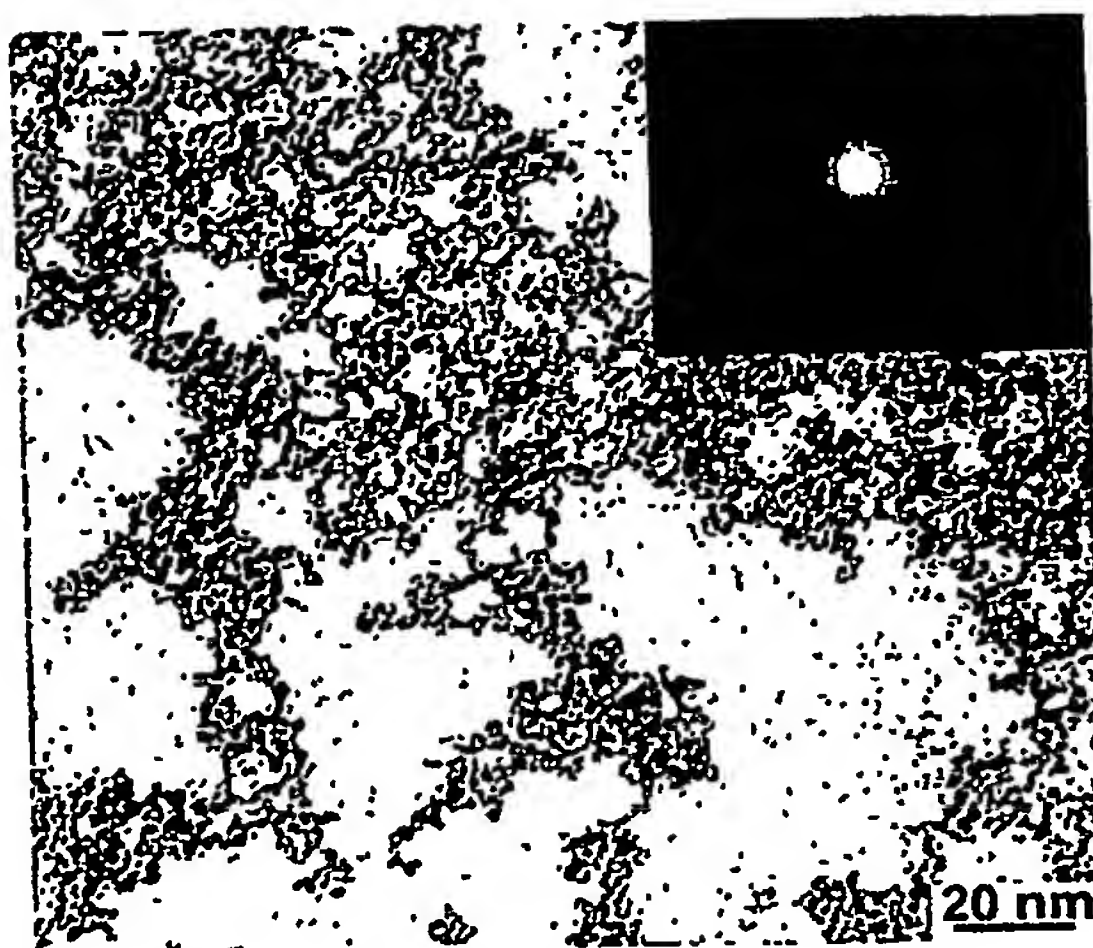


Fig 4  
TEM  
cds  
quantum dots

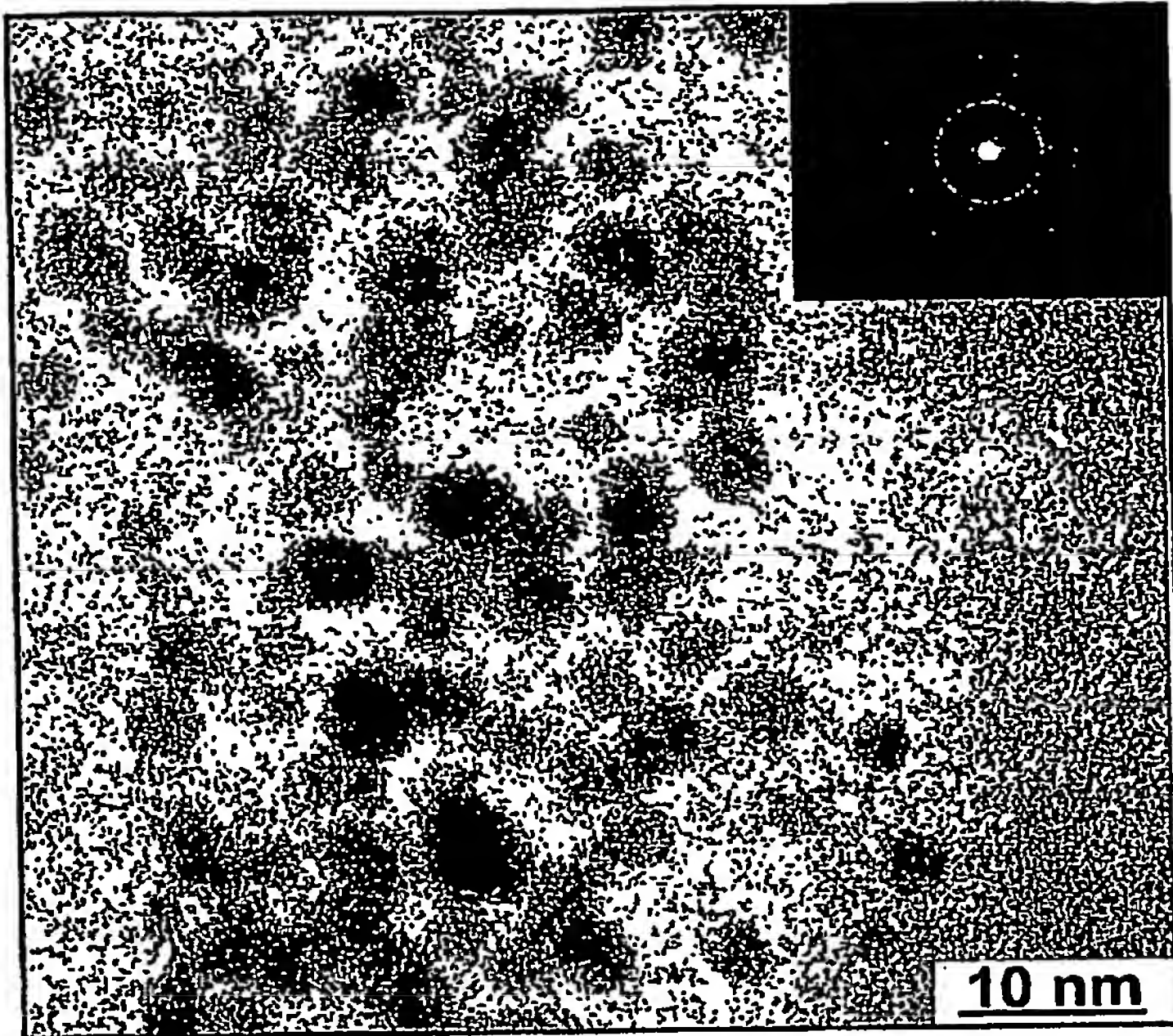
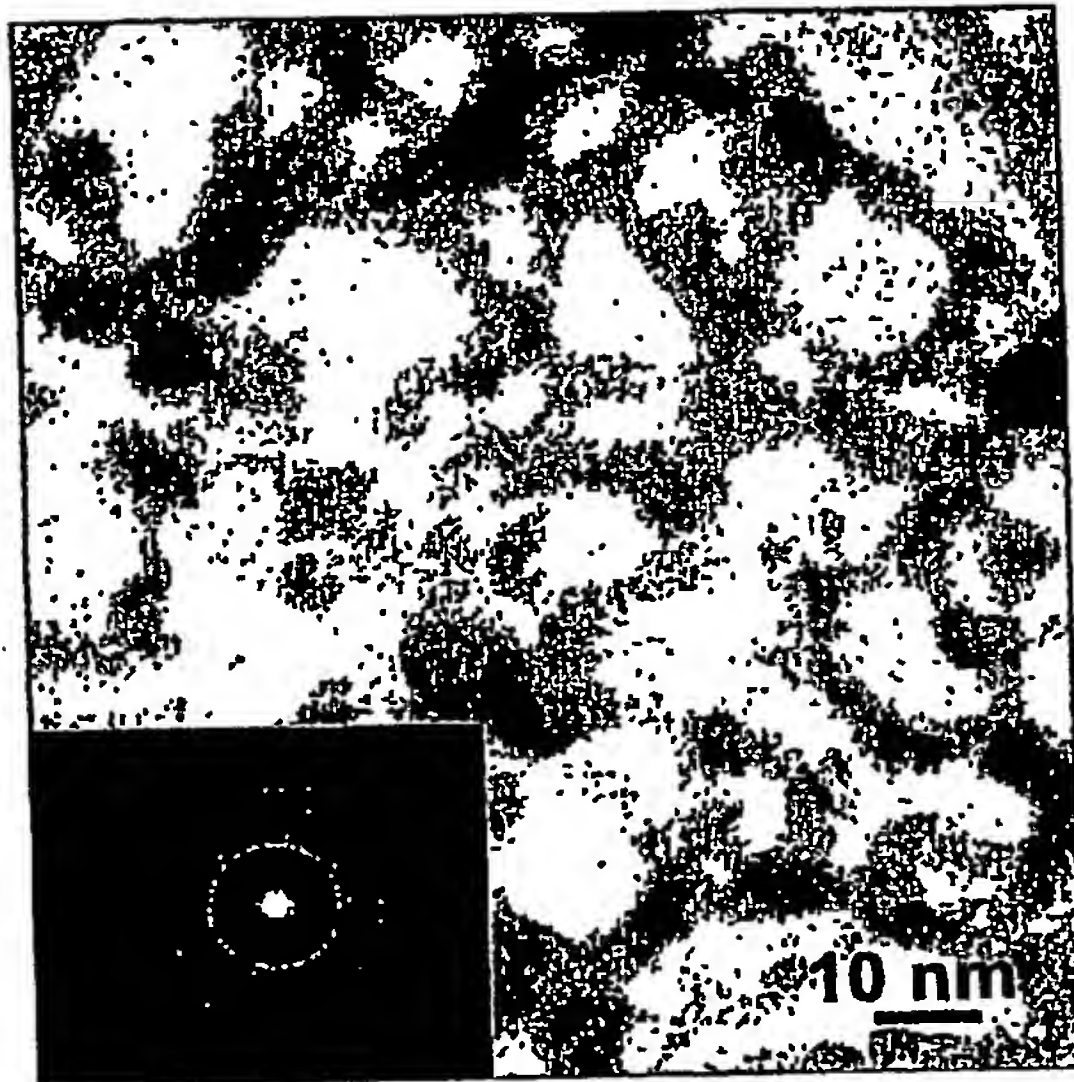


Fig 5.  
Nanoclusters

Fig 6  
TEM  
Nanowires



**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☒ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☒ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**